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13. ABSTRACT (Maximum 200 Words) Computational studies were carried out of the electronic structure and optical properties of chalcopyrite and defect chalcopyrite semiconductors. The second order nonlinear optical coefficients and frequency dependent response functions were calculated for the I-III-VI <sub>2</sub> chalcopyrites with I=Ag,Cu, III=Ga,In and VI=S, Se, Te. The superior properties of the tellurides were established. The band structure and effective masses of CdGeAs <sub>2</sub> were calculated including the effects of spin-orbit coupling. The band structures of the family of II-III <sub>2</sub> -VI <sub>4</sub> defect chalcopyrites with II=Zn,Cd,Hg, III=Al,Ga,In and VI=S,Se,Te with the thiogallate structure were calculated including gap corrections beyond the local density approximation. The optical anisotropy of CdSe optical reflectivity was calculated and compared with that in wurtzite GaN. The native point defects in ZnGeP <sub>2</sub> were studied. The energies for formation and charge occupation levels were determined for the V <sub>Zn</sub> , V <sub>Ge</sub> , Zn <sub>Ge</sub> and Ge <sub>Zn</sub> point defects and their relevance for the electron paramagnetic resonance spectra were determined.					
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Final Performance Report

FIRST-PRINCIPLES THEORY OF  
CHALCOPYRITES IN SUPPORT OF THEIR  
DEVELOPMENT FOR NONLINEAR OPTICAL  
APPLICATIONS

Grant No.: F49620-00-1-0037

Period of Performance: November 1, 2001 –April 30, 2003

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## 1 Objectives

The overall goal of the project is to perform first-principles studies of chalcopyrite semiconductors, in particular of properties relevant to their development for nonlinear optical applications. These properties include: the electronic band structures, the linear optical response functions, i.e. the optical dielectric function, the indices of refraction and birefringence, the nonlinear optical response, the point defects. While the project pays particular attention to the materials already under experimental investigation, such as  $\text{ZnGeP}_2$ ,  $\text{CdGeAs}_2$ ,  $\text{AgGaSe}_2$  and  $\text{AgGaTe}_2$ , it also investigates the trends of relevant properties in the entire family of chalcopyrite semiconductors and related materials.

## 2 Status of effort

The nonlinear optical properties of the I-III-VI<sub>2</sub> chalcopyrite family with I=Ag, Cu, III=Ga, In and VI=S, Se, Te were calculated. The trends of the nonlinear optical response in this family of materials were related to their electronic band structures. This complements an earlier study of the II-IV-V<sub>2</sub> chalcopyrite semiconductors. The band structure of  $\text{CdGeAs}_2$  was investigated, paying particular attention to the near band gap region. Effective masses were determined and the splittings of the near gap conduction and valence bands were related to optical spectroscopic investigations. Effects of spin-orbit coupling were determined. The band structures of a family of materials, known as defect chalcopyrites, or ordered vacancy compounds, with general formula unit II-III<sub>2</sub>-VI<sub>4</sub> were investigated. The anisotropy of the optical dielectric function of CdSe was studied and compared with that of GaN. Several native defects were studied in  $\text{ZnGeP}_2$ : the  $V_{\text{Zn}}$ ,  $V_{\text{Ge}}$  and the antisites  $\text{Ge}_{\text{Zn}}$  and  $\text{Zn}_{\text{Ge}}$ . Several topics deserving further study were determined and have become the subject of a continuation grant. F-49620-03-1-0010.

## 3 Accomplishments

### 3.1 Nonlinear optics of I-III-VI<sub>2</sub> chalcopyrites

The nonlinear optical response functions  $\chi^{(2)}(-2\omega, \omega, \omega)$  were determined for the entire family of I-III-VI<sub>2</sub> chalcopyrites with I=Ag, Cu, III=Ga, In, VI=S, Se, Te.[1] The most important conclusion from this work is the predicted superiority of the tellurides over the selenides in terms of  $\chi^{(2)}$ . While

generally, the observed trend of  $\chi^{(2)}$  is to increase with decreasing band gap, we found that several exceptions exist to this rule. For instance, starting from  $\text{AgGaSe}_2$ , the material most developed in this family at present, one might try to increase  $\chi^{(2)}$  either by replacing Ga by In or by replacing Se by Te. Both of these substitutions will decrease the band gap. We found however, that to increase  $\chi^{(2)}$  substituting Se by Te is far more effective than substituting Ga by In. Ultimately, it was shown that this is because the  $\chi^{(2)}$  is related to optical transitions throughout the Brillouin zone (BZ) and whereas the gap increases throughout the BZ by the  $\text{Se} \rightarrow \text{Te}$  substitution, it only increases near the zone center by the  $\text{Ga} \rightarrow \text{In}$  substitution. In terms of the figure of merit, FOM,  $[\chi^{(2)}]^2/n^3$  relevant to the power efficiency, the increase in  $\chi^{(2)}$  by a factor two with only a moderate increase in index of refraction  $n$  because only moderate decrease in gap, leads to a factor of three in going from  $\text{AgGaSe}_2$  to  $\text{AgGaTe}_2$ . At this moment, the higher  $\chi^{(2)}$  of  $\text{AgGaTe}_2$  still remains to be confirmed experimentally although work on  $\text{AgGaTe}_2$  crystal growth is on-going in a few laboratories.

In addition,  $\text{AgGaTe}_2$  was noted to have a positive birefringence and thus suitable alloys of  $\text{AgGaSe}_2$  (which has negative birefringence) with  $\text{AgGaTe}_2$  might be developed which have their birefringence tuned so as to achieve non critical phase matching (NCPM) for the frequency doubling of  $\text{CO}_2$  near 10  $\mu\text{m}$  lasers. Specifics of this alloy design were developed at Wright-Patterson Air Force Laboratory by Jonathan Goldstein and based on earlier work by M. C. Ohmer et al.[2] Our work, on the increase of  $\chi^{(2)}$  further strenghtens the case for development of  $\text{AgGaTe}_2$  and complements the AFRL work. The substitution by a heavier anion also will tend to push the optical phonon vibrational overtone absorption bands further into the far infra red, thus reducing the absorption in the region of the  $\text{CO}_2$  laser lines. It remains to be seen how much of an increase in  $\chi^{(2)}$  one will obtain in the alloys and whether or not these alloys can be developed with sufficient optical quality but this certainly makes the development of  $\text{AgGaTe}_2$  and  $\text{AgGa}(\text{Se}_{1-x}\text{Te}_x)_2$  an important goal for future chalcopyrite research. This is highly relevant for the Air Force needs in developing high-power tunable lasers in the mid-infrared range for infrared counter measures and surveillance.

Our work also showed that Cu substitution for Ag will not improve  $\chi^{(2)}$  in spite of the fact that it generally reduces the band gaps slightly. This was related to the fact that in Cu-III-VI<sub>2</sub> compounds we found there to be a stronger compensation of intra band and interband processes in the  $\chi^{(2)}$  response function. The separation of these two processes in the calculation was thus found to have important practical consequences.

### 3.2 Band structure of CdGeAs<sub>2</sub>

CdGeAs<sub>2</sub> has been identified as an important target material for nonlinear optical conversion, in particular for the frequency doubling of CO<sub>2</sub> laser lines. Compared to its predecessor ZnGeP<sub>2</sub>, it has the advantage of a lower optical absorption in the CO<sub>2</sub> laser line range because the multiple phonon lines are farther in the infrared because of the heavier As than P anion. It also has a record  $\chi^{(2)}$  value. Compared to AgGaSe<sub>2</sub> and AgGaTe<sub>2</sub> it has a higher thermal conductivity and much higher  $\chi^{(2)}$ . On the other hand, its transparency is still far from that in the I-III-VI<sub>2</sub> chalcopyrites because of unwanted defect absorption. Its band gap on the other hand is rather small (0.65 eV) making it less suitable for OPO applications with pumps near 1  $\mu$ m. In work prior to the present grant,[3] we had calculated the band structure and  $\chi^{(2)}$  and explained the reason for the record  $\chi^{(2)}$  in terms of the very small inter band contribution to  $\chi^{(2)}$ , which, compared to other II-IV-V<sub>2</sub> chalcopyrites, usually compensates the useful intraband contribution to a significant extent.

Several questions however remained unclear about the details of the band structure of this material, in particular near the fundamental band gap. With support from this grant, we investigated the effects of spin-orbit coupling, crystal field anisotropy and quasi particle corrections on the band structure of CdGeAs<sub>2</sub>. [4] The effects of the Cd *d*-band on the near the gap energy levels were investigated. In terms of the optical spectra it was pointed out that some indirect transitions are occurring near the pseudodirect transitions and require a revision of the interpretation of the experimental data. The effective masses of the conduction and valence band were determined. In fact, the symmetry invariant theory of Pikus and Bir was extended to the chalcopyrite  $D_{2d}$  symmetry and a generalization of the Kohn-Luttinger effective mass Hamiltonian description of the valence band manifold was obtained and its parameters determined. This may form the basis for future investigations of excitonic effects and shallow acceptor states. This work was of direct relevance to experimental work on-going at AFRL and Wright laboratory by S. R. Smith et al. [5]

### 3.3 Defect Chalcopyrites

The defect chalcopyrites form a new class of compounds, related to chalcopyrites, which can be described as ordered vacancy compounds. Starting from a I-III-VI<sub>2</sub> chalcopyrite, we may consider a doubled unit cell and replace the two group I atoms by a single group II atom and a vacancy. If these

vacancies occur in an ordered array, a symmetry lowering of the chalcopyrite symmetry occurs and the so-called defect chalcopyrite structure results. It is important to note that this substitution still satisfies the octet rule and thus a semiconductor results.

We performed band structure calculations for the 22 members of this family for which crystal structure information was available.[6] The band gaps were corrected with a beyond LDA correction based on their relation to the parent chalcopyrite and grand parent II-VI compounds. Good agreement with experimental data was obtained in the cases where experimental data were available. For a number of other compounds, our work provides predictions. We found that the d-bands of the II elements play an important role. In comparison with the II-VI compounds the I-III-VI<sub>2</sub> compounds have generally lower band gaps because of the higher lying group I-d bands which hybridize significantly with the VI-p valence bands and push up the valence band maximum. By going back to II elements, this effect is reduced, re-opening the band gap. While generally wider band gaps lead to smaller  $\chi^{(2)}$  this rule only is valid within a family of closely related compounds. For instance II-VI's have larger  $\chi^{(2)}$  than the corresponding I-III-VI<sub>2</sub> materials. For some defect chalcopyrites, large  $\chi^{(2)}$  have been reported and the bond charge model also predicts a larger  $\chi^{(2)}$  due to the II-VI bonds as opposed to I-VI bonds.[7, 8] Also, the larger band gap may be an advantage in terms of a wider transparency range. Additional work to determine the  $\chi^{(2)}$  directly has been postponed to the continuation grant F-49620-03-1-0010 because it requires adjusting the computer codes for  $\chi^{(2)}$  for the more complex crystal structure. These materials have previously been studied primarily in the former Soviet Union. Some of the recent work has been supported by an AFRL cooperation to convert former Soviet defense work into civilian research and has been coordinated by N. Fernelius at Wright Patterson AFRL. Our work should be relevant to this effort.

### 3.4 Optical Anisotropy in CdSe

While somewhat further removed from the main topic, wurtzite crystals such as CdSe are possibly useful for nonlinear optics because of their anisotropy of the dielectric function. Our main interest in this material arose from a conjecture by Benedict et al. [9] that there would be an interesting similarity in the anisotropy of the UV optical reflectivity with that of GaN. GaN also has the wurtzite structure and is, as is well known, mainly studied for the development of optoelectronic applications such as blue-UV lasers and blue and white LEDs. This work is also of interest to the AFOSR and since we

had prior experience on this material, we decided to investigate this issue of the UV reflectivity anisotropy.

It was found that there are indeed similarities but also interesting differences and the interpretation of the spectral features proposed earlier was found by our work to be incorrect. Our work[10] utilizes a detailed decomposition of the dielectric function into its individual band-to-band components and also considers continuum excitonic effects in assigning the various features.

### 3.5 Point defects in ZnGeP<sub>2</sub>

Point defects play an important role in chalcopyrite semiconductors and limit their present performance in nonlinear optical applications by introducing unwanted optical absorption bands near the band edges. This unwanted optical absorption leads to heating of the crystal and thus limits the power at which the devices can be operated. For future improvements it is important to identify the nature of these defects. In ZnGeP<sub>2</sub>, an important question is whether the dominant defects related to slight deviations from perfect stoichiometry are antisites or vacancies. Recent work has emphasized the importance of the Zn vacancy whereas older work emphasized the cation-antisite disorder. Our work was primarily geared towards a study of the  $V_{Zn}$  in connection with the extensive EPR studies that are available on this system.

The work on defects was primarily carried out during the last year of the grant. Therefore some more detail is provided here than on the other topics, which were covered in the previous year Progress Reports.

Several hurdles had to be overcome to make this study possible. First of all, in order to deal with charged states of the defects, modifications had to be made to the computer program to deal with the neutralizing uniform background charge density. Secondly, the program had to be ported to a parallel supercomputer because the computer resources required exceeded the capabilities of our local facilities. The methodology used is a full-potential linear muffin-tin orbital method including, automatic structural relaxation by calculating the interatomic forces. The density functional method provides the underlying conceptual framework as for our other studies. The defects are modelled in periodic boundary conditions using 64-128 atom supercells. The code was parallelized using the message passing interface (MPI) by a collaboration with A. T. Paxton at the Queens University of Belfast and run at the Ohio Supercomputer Center (OSC).

After initial testing of the codes, a substantial amount of time was spent

on the study of the  $V_{Zn}$ . In fact, one of the main problems was that our results appeared to be in disagreement with some of the EPR results. One of the main conclusions resulting from the EPR-ENDOR investigations is that the wavefunction of the unpaired electron observed in the EPR spin 1/2 spectrum is primarily located on two equivalent Phosphor atoms rather than four as one would expect for an unrelaxed Zn-vacancy. This was attributed by the experimentalists to a symmetry breaking relaxation of the defect and in fact, the fact that large relaxations are required to explain the geometry features extractable from the hyperfine splittings led to the identification of this spectrum to the  $V_{Zn}^-$  defect. Our calculations, however, indicated that such symmetry breaking does not occur for the  $V_{Zn}$ , neither in the neutral nor in the negatively charged state. Since symmetry breaking relaxations do not occur spontaneously in the calculation if one starts from a symmetric saddlepoint, several attempts were made to study different initial positions of the defect in order to induce a symmetry breaking. However, invariably, the structure returned to a symmetric configurations when allowed to relax the atomic positions so as to minimize the total energy of the defect. In the end we had to accept our computational result as being the correct one and conclude that the experimental EPR spectrum cannot be attributed to a  $V_{Zn}^-$  center. Several alternatives were then studied as well as results obtained on other defects in order to build up a database of the main native point defect properties. The  $Zn_{Ge}$  antisite had been considered as an alternative candidate for the acceptor like EPR centrum but also was found to retain the crystal's  $D_{2h}$  symmetry. The  $Ge_{Zn}$  defect was studied because data on this defect are also available and to complete this set, we also studied the  $V_{Ge}$ .

The Gibbs free energy of a defect  $\alpha$  is given by

$$\Delta\Omega(\alpha, q) = E_{sc}(\alpha) - E_{sc}(0) - \sum_i \Delta n_i \mu_i + q\mu_e, \quad (1)$$

where  $E_{sc}(\alpha)$ ,  $E_{sc}(0)$  are the energies of the supercell containing the defect and that of the perfect crystal respectively, and  $\Delta n_i$  is the change in number of atoms of a given species  $i$  in forming the defect and  $\mu_i$  their chemical potential,  $q$  is the charge state and  $\mu_e$  the chemical potential of the electron or Fermi level on an absolute scale. For instance, in removing a Zn to form the Zn vacancy, a term  $\mu_{Zn}$  is added to the supercell total energy difference. In forming a  $Zn_{Ge}$  antisite, a Ge is removed and a Zn added, so the chemical potential terms in Eq. (1) are  $-\mu_{Zn} + \mu_{Ge}$ . The chemical potential of the electron is  $\mu_e = E_{vbm} + E_F$  where  $E_{vbm}$  is the one-electron energy of the valence band maximum of the perfect crystal relative to the average



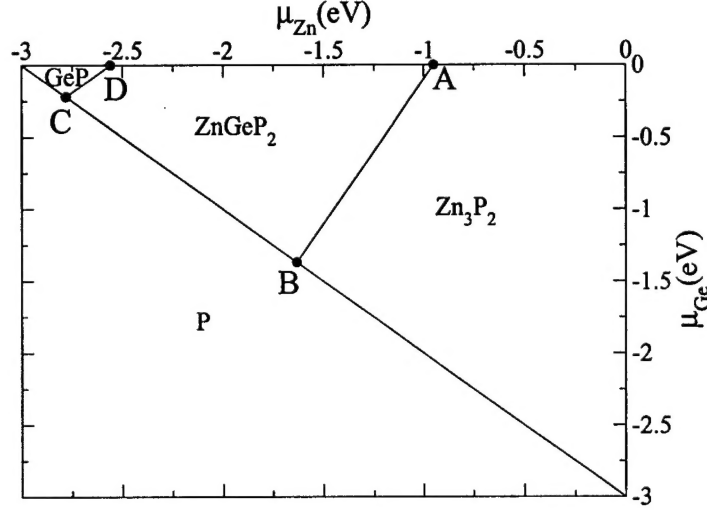


Figure 1: The allowed range of Zn and Ge chemical potentials is indicated by the region labeled  $\text{ZnGeP}_2$ . Above  $\mu_{\text{Ge}} = 0$ , Ge would precipitate, below the line BC, P will precipitate, to the right of AB,  $\text{Zn}_3\text{P}_2$  will precipitate, while to the left of CD GeP would precipitate.

electrostatic potential far away from the defect in the defect containing supercell. It can alternatively be calculated from a total energy difference for the perfect crystal or by aligning a local reference on an atom far away from the defect with that in the perfect crystal.

The range of applicable chemical potentials of the atoms is limited by conditions of thermodynamic equilibrium and is summarized in Fig. 1

As formation energies for the neutral states at three representative chemical potential conditions, we obtain the results of Table 1. The labels A, B, C refer back to Fig. 1 and correspond to Zn and Ge-rich, Ge-poor, and Zn-poor conditions respectively. Most recent experimental results are believed to correspond to Zn-poor conditions.

One can see that for Zn-rich and Ge-rich conditions the antisites have lower formation energies than the vacancies. However for Zn-rich conditions, the lowest energy defects are the  $\text{Ge}_{\text{Zn}}$  site and the  $V_{\text{Zn}}$ . The  $V_{\text{Ge}}$  is a high energy defect under all circumstances. This is consistent with the Ge-P bond being stronger in  $\text{ZnGeP}_2$  than the Zn-P bond as indicated by the slight relaxation of the P toward Ge in the crystal structure. In fact, EPR

Table 1: Energies of formation of native point defects in  $\text{ZnGeP}_2$  (in eV) in the neutral state and for different values of the chemical potentials as indicated.

	A	B	D
$\mu_{\text{Zn}}$	-0.95	-1.63	-2.56
$\mu_{\text{Ge}}$	0	-1.37	0
$\Delta\Omega(V_{\text{Zn}})$	2.39	1.71	0.78
$\Delta\Omega(V_{\text{Ge}})$	4.23	2.86	4.23
$\Delta\Omega(\text{Zn}_{\text{Ge}})$	1.74	1.05	3.35
$\Delta\Omega(\text{Ge}_{\text{Zn}})$	1.41	2.10	-0.20

spectra associated with both the  $V_{\text{Zn}}$ [11, 12, 13] and the  $\text{Ge}_{\text{Zn}}$  [14] are known.

From the charge states for the  $V_{\text{Zn}}$  shown in Fig. 2, as function of Fermi level position, we can see that the vacancy goes from a neutral to a singly negative charge state very close above the VBM and to a double negative charge state at about 0.5 eV above the VBM. This means that the  $V_{\text{Zn}}$  is a shallow double acceptor. This is confirmed by inspecting the one-electron eigenvalue at the  $\Gamma$ -point of the supercell band structure, as shown in Fig. 3.

This figure shows the first empty state for the neutral  $V_{\text{Zn}}$  to be nondegenerate and to lie only 95 meV above the last completely filled doublet. The dangling bonds of the P surrounding the vacancy form a deep resonance of  $a_1$  symmetry and a  $t_2$  symmetry level in the gap in the symmetry group  $T_d$ . This  $t_2$  level splits into a doubly degenerate  $e$ -symmetry level and an  $a_1$  symmetry level for the tetragonal  $D_{2h}$  symmetry of the chalcopyrite, which is also maintained for the defect. This is illustrated schematically in Fig. 4.

The  $e$ -level at  $\Gamma$  is found to lie slightly above the valence band maximum, when estimating the latter from the perfect crystal and the position of the local average electrostatic potential far away from the vacancy but when including its broadening in to a band by the spurious intercell interaction, one would find it to be resonant with the valence band as indicated by the fact that positive charge states are not found to be the minimum energy for any Fermi level position in the gap.

The shallow nature of the defects is consistent with the absence of symmetry breaking relaxations. In fact, the defect level in the gap, has  $a_1$  symmetry, and is thus non-degenerate, apart from spin. This means that there is no Jahn-Teller symmetry breaking expected. If, the order of the

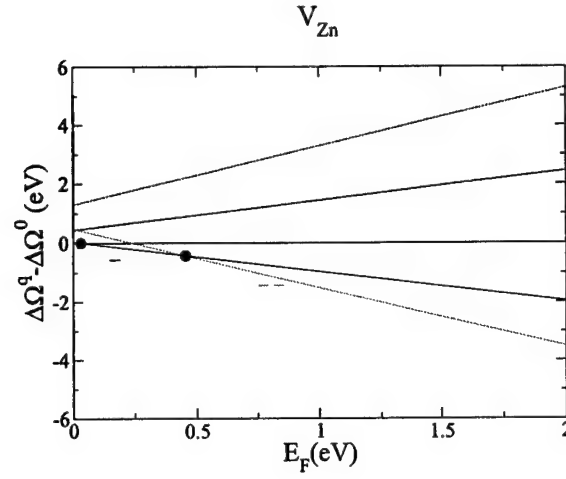


Figure 2: Energy of formation of different charge states of the  $V_{Zn}$  in  $ZnGeP_2$ .

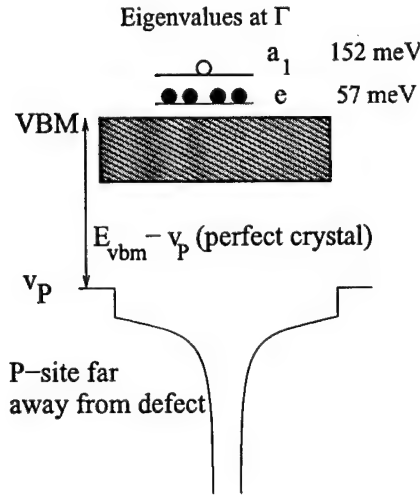
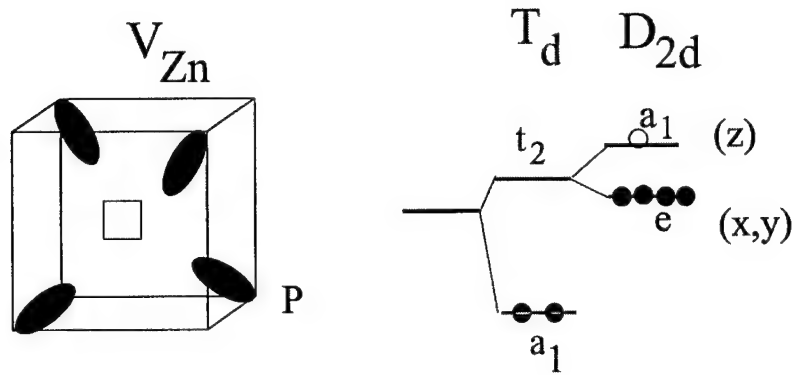


Figure 3: Energy levels at  $\Gamma$  supercell relative to the valence band maximum (VBM) and the crystal potential. The crystal potential is a schematic representation only, illustrating the alignment procedure used to determine the VBM.



number of electrons:  $4 \times (3/2) = 6$

Figure 4: Dangling bond model of the  $V_{Zn}$  and the splitting of the levels and their filling for the neutral state.

$a_1$  and  $e$ -levels were reversed, one could expect a lowering of the energy by breaking the symmetry such that the  $e$ -level splits. We found that the order of the  $e$ - and  $a_1$  states is related to the local  $c/a$  ratio. Local in the sense that it might be different near the vacancy than in the crystal overall. We tried if stretching the coordinates locally so as to interchange the  $e$  and  $a_1$  states would lead perhaps to a metastable state from which a symmetry broken new ground state with localization on two P would result. However, it was found that this requires an unrealistically large stretching of the local geometry and costs too large an energy and still does not lead to a symmetry broken relaxed state.

Similarly, we find that the  $Zn_{Ge}$  defect is also a double acceptor. Here we find the negative charge state to lie slightly deeper at about 0.1 eV as shown in Fig. 5. Nevertheless, this defect also stays symmetric and can be ruled out as a candidate for the AL1 EPR spectrum.

The  $V_{Ge}$  is a quadruple acceptor, although we have so far only calculated its first two negative states. The  $Ge_{Zn}$  on the other hand is found to be a double donor as shown in Fig. 6. An EPR spectrum with the single positive state of this defect is found to occur upon illumination of  $ZnGeP_2$  with light above a certain threshold frequency.

The energy levels in the gap are summarized in Fig. 7.

As already mentioned, the  $V_{Zn}^-$  has in the past been assigned to be

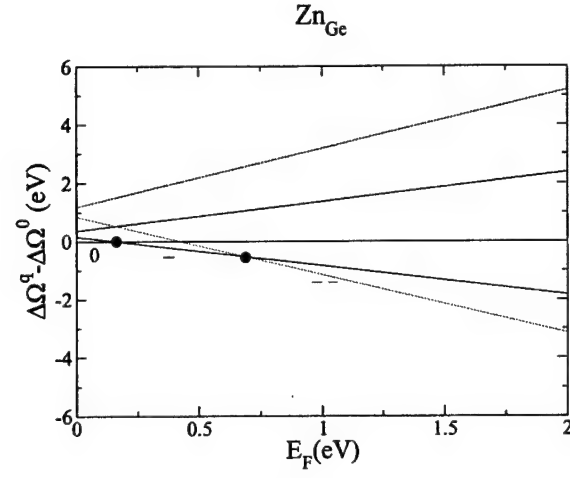


Figure 5: Formation energies for different charge states of the  $Zn_{Ge}$  antisite defect.

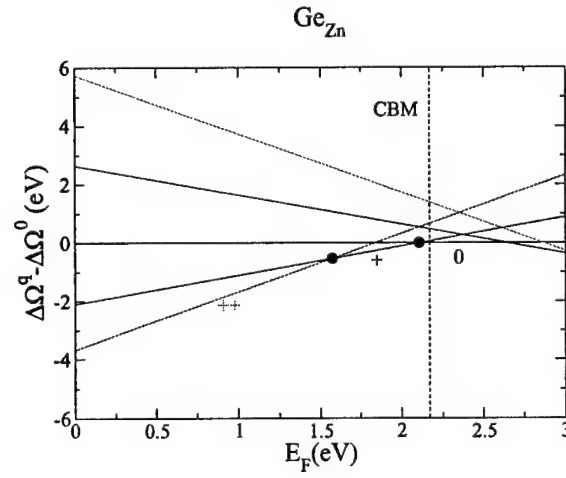


Figure 6: Formation energies for different charge states of the  $Ge_{Zn}$  antisite defect.

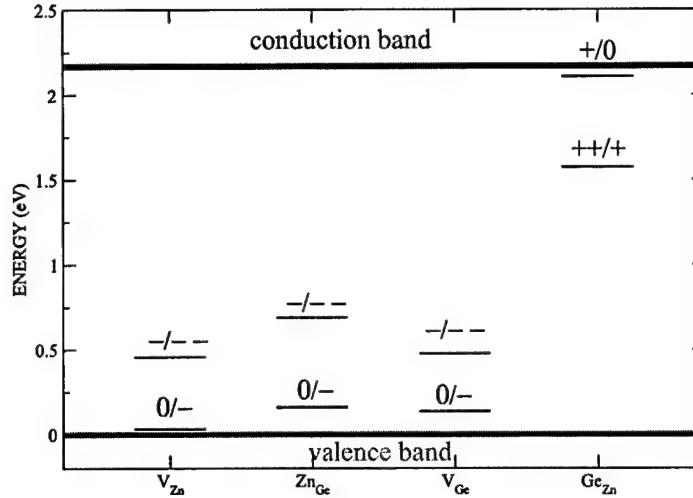


Figure 7: Summary of occupation levels in the gap for various native point defects in ZnGeP<sub>2</sub>.

responsible for the dominant EPR signal in as grown ZnGeP<sub>2</sub> crystals, labeled originally the AL1 defect.[11, 12] However, our results are ruling out this assignment. In fact, the hyperfine structure of the EPR-ENDOR studies[12, 13] reveal that the defect wave function involves primarily two equivalent neighboring P atoms. Our results for the V<sub>Zn</sub> indicate that the four P are equivalent. Even if symmetry breaking distortions were allowed the defect always returned to the  $D_{2h}$  symmetric situation after relaxation. The Zn<sub>Ge</sub> and V<sub>Ge</sub> can also be ruled out because they all remain symmetric. The Ge<sub>Zn</sub> is a donor rather than an acceptor and corresponds to an other EPR center. This indicates the need for studying defect complexes as alternative candidates for the EPR centers. This work has been taken up in the continuation grant F-49620-03-1-0010 and will be reported on in the latter's first year progress report.

### 3.6 Computer Code development

It is impractical here to provide computer code utilized in this work because it is excessively long. The modifications we made are incorporated into a package of lnto codes which is not being commercially or freely distributed but rather on the basis of collaborations. We are willing to make our code

contributions available upon request.

The basic code used in this work for the full -potential method is described in ref. [15]. The new aspects introduced during this work have to do with including the neutralizing background in the charge density and require small modifications in a few subroutines only.

## 4 Personnel Supported

The project has provided summer salary for the PI Walter R. L. Lambrecht and part time support for a postdoctoral Research Associate Dr. M. S. Miao. Dr. Miao has mainly worked on methodological aspects of the project, involving the defect calculations. It has provided mainly support for several graduate students: Mr. Xiaoshu Jiang has worked exclusively on this project and is responsible for most of the work on the point defects and the defect chalcopyrites. The work on CdSe was in part carried out by Mrs. Margarita Prikhodko, another graduate student.

## 5 Publications

1. S. N. Rashkeev and W. R. L. Lambrecht, Second harmonic generation of I-III-VI<sub>2</sub> chalcopyrite semiconductors: Effects of chemical substitutions, *Phys. Rev. B* **63**, 165212 (2001)
2. S. Limpijumnong and W. R. L. Lambrecht, Band structure of CdGeAs<sub>2</sub> near the fundamental gap, *Phys. Rev. B*, **65**, 075207 (2002).
3. W. R. L. Lambrecht and M. Prikhodko, Anisotropy of UV-reflectivity in wurtzite crystals: a comparison between GaN and CdSe, *Solid State Commun.* **121**, 549-554 (2002)
4. W. R. L. Lambrecht and S. N. Rashkeev, First-principles calculations of second-order optical response functions in chalcopyrite semiconductors, *J. Phys. Chem. Solids*, **64**, 1615 (2003).
5. Xiaoshu Jiang and Walter R. L. Lambrecht, Electronic band structure of defect chalcopyrites, *Bull. Am. Phys. Soc.* **46**, D40.152, (2001).
6. Xiaoshu Jiang and Walter R. L. Lambrecht, Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula II-III<sub>2</sub>-VI<sub>4</sub>, submitted to *Phys. Rev. B*

7. Xiaoshu Jiang, M. S. Miao and Walter R. L. Lambrecht, Electronic structure of native point defects in  $\text{ZnGeP}_2$ , in preparation for MRS Fall Meeting Symposium.

## 6 Interactions/Transitions

### a. Presentations at conferences.

- APS March Meeting 2001, Seattle, Xiaoshu Jiang and Walter R. L. Lambrecht, Electronic band structure of defect chalcopyrites,
- ICTMC13, Paris Oct. 14-18, 2002, Walter R. L. Lambrecht and S. N. Rashkeev, First-principles calculations of second-order optical response functions in chalcopyrite semiconductors, invited talk.
- AFOSR Semiconductor Program Review, Lancaster, PA, June 18-20 (2002), First principles Theory of Chalcopyrites in Support of their Development for NLO Applications, invited talk
- AFOSR Semiconductor Program Review, Williamsburg, VA, June , 9-11 June 2003, Walter R. L. Lambrecht, Nonlinear optics and defects in Chalcopyrite Semiconductors

### b. Collaborations

We enjoyed continuing collaborations with some of our prior coworkers. Dr. Sergey Rashkeev was a previous postdoctoral associate in my group and responsible for the development of the nonlinear optical calculations. We continued collaborating with him after his move to Vanderbilt University as a Research Professor.

Dr. Sukit Limpijumnong was a former graduate student in my group and collaborated on the study of  $\text{CdGeAs}_2$ . He currently is at Suranaree University of Technology in Thailand.

We also enjoyed useful interactions with several researchers from the AFRL at Wright-Patterson and Wright State University: M. C. Ohmer, S. R. Smith, J. Goldstein, F. Smulowicz.

We also exchanged information with experimentalists at the university of West Virginia in Morgantown: L. Halliburton and N. C. Giles, in particular in regards to the EPR studies in  $\text{ZnGeP}_2$  and with Arnold Burger at Fisk University relating to  $\text{AgGaTe}_2$  crystal growth and with W. Gehlhof and A. Hoffman at the Technical University in Berlin relating to their optically induced EPR studies.



### c. Transitions

Nothing to report.

## 7 New discoveries

No patent applications were submitted from this work.

## 8 Honors/Awards

The PI was elected Fellow of the American Physical Society in 2003 among other for his work on nonlinear optics in chalcopyrite semiconductors related to this grant.

The work on nonlinear optics in chalcopyrites led to an invited talk at the 13th International Conference on Ternary and Multinary Compounds in Paris, October 14-18th.

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